Armed Services Technical Information Agency

AD
44956

UNCLASSIFIED

Physics   Translated from Doklady Akademii Nauk SSSR, **92**, 29-32 (1953)

The Magnitude of the Optical Anisotropy
of the Benzene and Carbon Disulfide Molecules
as Determined by Light Scattering in Solutions

M. F. Vuks and V. I. Yelfimov

Analysis of experimental data on the scattering of light in liquids has shown that deviation of the intensity of the anisotropic scattering from the quantity calculated from the gas theory is due to the presence in the liquid of short-range orientative order. From this point of view it has been possible to explain the experimentally observed change in intensity of the anisotropic light scattering in liquids during heating by assuming that the existing short-range order is gradually destroyed.

In order to make a further, more thorough examination of these assumptions, we undertook an investigation of the intensity of anistropic light scattering in liquids, inasmuch as we must expect that the process of solution should lead to the same result as the process of heating. We should find a decrease in the orienting interaction and a destruction of orientative order.

Together with I. A. Bogdanov, we measured the intensity of the anisotropic scattering for a series of solutions of nitrobenzene, phenol, and aniline. These measurements justified our assumptions. They showed that the intensity of the anisotropic scattering of solutions of small concentration is determined, if we exclude certain particular cases, by the optical anisotropy of the isolated molecules of the dissolved substance, and can be represented in the form of a sum of two parts—scattering from the free molecules of the solute according to gas theory, and the scattering from the solvent considered as a pure liquid.

$$R_{an} = R'_{an} + R''_{an} = \frac{8\pi^4}{\lambda^4} \frac{13}{45} \left(\frac{n^2+2}{3}\right)^2 \left(N'\gamma^2 + N''\gamma^2_{eff}\right). \tag{1}$$

Here R_{an} is the constant for anisotropic Rayleigh scattering of the solution; R'_{an} and R''_{an} are the constants for the anisotropic scattering by the solute molecules and those of the solvent; n is the index of refraction of the solution; N' and N'' are the number of molecules of the solute and solvent per cm^3 of solution; γ^2 is the optical anisotropy of the isolated molecules of the solute; and γ^2_{eff} is the effective optical anisotropy of the molecules of the pure solvent determined by the formula (2) for the pure liquid.

$$R_{an} = \frac{8\pi^4}{\lambda^4} \frac{13}{45} \left(\frac{n^2+2}{3}\right)^2 N \gamma^2_{eff}. \tag{2}$$

The significance of the investigation of the light scattering in solutions is not limited by what was said at the beginning. By this investigation we

have at the same time established a new method for determining the optical anisotropy of molecules.

It is easy to understand that liquids with as small an optical anisotropy as possible should be taken as solvent. The smaller the anisotropy of the scattering of the solvent, the smaller the concentration of the solute that can be examined. One should take, if possible, such concentrations that the scattering from the solute molecules is larger than that of the solvent.

In the present paper we are extending the investigations begun earlier to new specimens — benzene and carbon disulfide. These substances are of considerable interest since the optical anisotropy of benzene and carbon disulfide molecules is quite well known on the basis of the data on light scattering and the Kerr effect in vapors. Thus our results here may be compared with those obtained in these previous investigations.
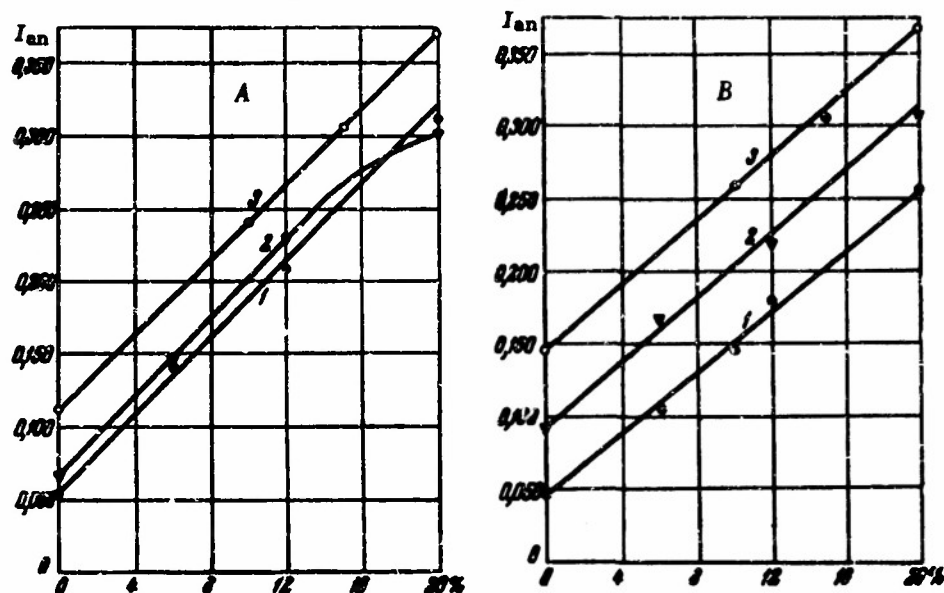

Fig. 1. Intensity of anisotropic scattering of benzene solutions. A: 1 in carbon tetrachloride, 2 in cyclohexane, 3 in heptane. B: 1 in alcohol, 2 in ether, 3 in acetone.

As solvents we used the same liquids we used previously: carbon tetrachloride, cyclohexane, heptane, ordinary alcohol, ether, and acetone. In addition, carbon disulfide was investigated in benzene solutions. Benzene was investigated in concentrations from 6 to 20 percent, carbon disulfide from 3 to 10 percent. The density and the index of refraction were calculated by the additivity rule. We shall not go into the details of the experimental procedure since it is similar in all respects to that described previously.[1]

Let us consider our results, which are presented in the graphs in Figs. 1 and 2. The abscissa represents the volume concentrations of benzene and carbon disulfide, and the ordinate is used to represent the intensity of the anisotropic scattering with respect to benzene. In order to obtain the scattering constant, we must multiply the plotted numbers by 5.5×10^{-6}.

According to the theoretical formula (1), the curves of the dependence of the intensity on concentration must deviate from the straight line, bending slightly upward, by approximately 1 percent for benzene solutions and by 2 percent for carbon disulfide solutions.

For benzene we found in five solvents a practically linear dependence for the whole range of the concentrations used. Only in the sixth solvent,

cyclohexane, did the last point fell slightly below the straight line. Table I gives the magnitude of the optical anisotropy of benzene molecules calculated from the straight-line portion according to formula (1).

Table I. Values for the optical molecular anisotropy of benzene and carbon disulfide determined by light scattering in solutions ($\gamma^2 \times 10^{48}$).

Substance in solution	Solvents								From light scattering and Kerr effect
	CCl_4	cyclohexane	heptane	alcohol	ether	acetone	benzene	average	
Benzene . .	31	34	35	(28)	31	31	—	33	35,5
Carbon di-sulfide . .	88	91	92	88	92	91	94	91	92

The experimental points for solutions of carbon disulfide also fall very well on straight lines. The values obtained for the optical anisotropy of molecules of carbon disulfide are shown in Table I. In addition, Table I contains the anisotropy of the carbon disulfide molecule in a benzene solution found in the investigation of a 10 percent solution. The intensity of the anisotropy of the scattering was 1.57.
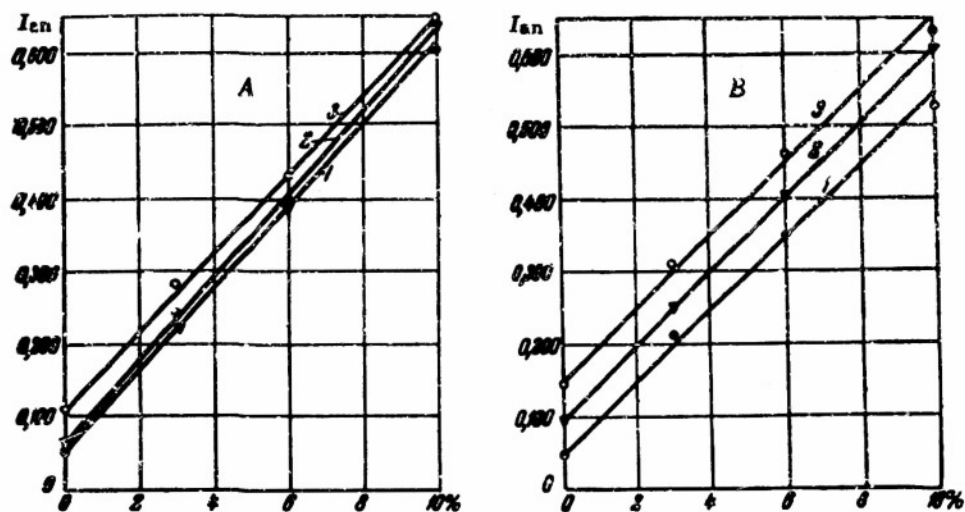

Fig. 2. Intensity of anisotropic scattering of solutions of carbon disulfide. A: 1 in carbon tetrachloride (points), 2 in cyclohexane (triangles), 3 in heptane. B: 1 in alcohol, 2 in ether, 3 in acetone.

All the results cited were obtained at 20 degrees. Many solutions were heated to 50, and some to 80 degrees. Measurements showed that during heating there is little change in the intensity of the anisotropic scattering. These changes take place in rather good agreement with the formula (1) so that the optical anisotropy of molecules in solution remains practically unchanged.

As the data in Table I show, the magnitude of the optical anisotropy of the benzene molecule in different solvents varies from 31 to 35×10^{-48}, with the exception of the solutions in alcohol. The average value is 33×10^{-48}. The anisotropy of the molecules of carbon disulfide varies from 88 to 94 $\times 10^{-48}$, with the average at 91×10^{-48}.

It is of interest to compare our data with the data obtained from investigation of the scattering of light and the Kerr phenomenon of benzene and carbon disulfide vapors. The values given[2] for the principal polarizabilities of benzene and carbon disulfide molecules are 63.5, 123.1, 123.1 × 10^{-25} and 55.4, 151.4, 151.4 × 10^{-25}. From these we obtain for the optical anisotropy of the benzene and carbon disulfide molecules the values 3.5 × 10^{-48} and 92 × 10^{-48}, respectively. Our data agree sufficiently well with the latter, particularly in the case of carbon disulfide.

Some solvents seem to exert a small influence on the optical anisotropy of the molecules of the solute. Thus, for instance, in alcohol solution the anisotropy of the benzene molecules is slightly smaller than in other solvents. We obtained in benzene the value of 28 × 10^{-48}. This deviation is obviously outside the limits of experimental error. In this case we are inclined to attribute the lowered value for the anisotropy to the incomplete molecular solubility of benzene in alcohol.

From the experimental data reported we can draw the following conclusions:

(1) The intensity of the anisotropy of the Rayleigh scattering of light in dilute solutions is determined, in suitable choice of solvent, by the anisotropy of the isolated molecules of the solute and the effective anisotropy in the liquid state of the molecules of the solvent, and can be calculated by a formula analogous to that for gases.

(2) The measurement of the intensity of the anisotropic part of the Rayleigh scattering of solutions permits us to determine the optical anisotropy of the molecules of the dissolved substance. This constitutes a new method for the determination of the optical anisotropy of molecules.

(3) The experimental data obtained in this investigation confirm the assumption that the deviations of the intensity of anisotropy of light scattering in pure liquids from the quantities given by the formula derived for gases are due to the presence of short-range orientative order.

[1] M. F. Vuks and I. I. Bilenko, Zhur. eksptl. i teort. fiz., 23, 105 (1952).

[2] G. Styuart [Stuart], Struktura molekul [Molecular Structure], 1937.

Armed Services Technical Information Agency

AD

44956

UNCLASSIFIED